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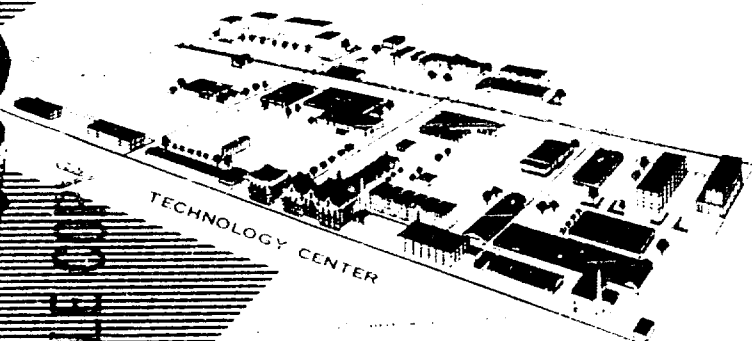
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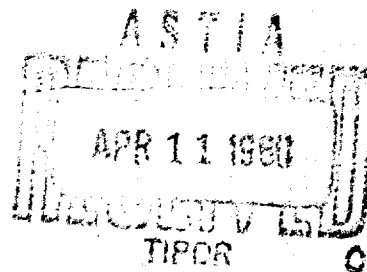
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A MECHANISM FOR STRESS-CORROSION EMBRITTLEMENT

Office of Naval Research
Washington 25, D. C.

Contract No. Nonr-2602(00)



ON A SURFACE ENERGY MECHANISM
FOR STRESS-CORROSION CRACKING

ABSTRACT

It has been demonstrated that stress-corrosion cracks can be initiated on continuous loading in a suitable medium. Results are shown for stainless steel immersed in boiling MgCl_2 solution and for a Mg-6%Al alloy in aqueous $\text{NaCl-K}_2\text{CrO}_4$ solution at room temperature. This behavior has been used to analyze the stress-corrosion cracking process in terms of the dislocation theory of brittle fracture. It is proposed that the mechanism of cracking originates from a condition of reduced surface energy brought about by adsorption of some ion species from the surrounding medium. An analysis of the grain size dependence of the fracture initiation stress in the stress-corrosion media leads to estimates of reduced surface energies of the order of $100\text{-}200 \text{ ergs/cm}^2$.

ON A SURFACE ENERGY MECHANISM **FOR STRESS-CORROSION CRACKING**

by

E. G. Coleman, D. Weinstein, and W. Rostoker*

Embrittlement by stress corrosion is most commonly observed in the form of time-dependent brittle fracture when a metal or alloy is subjected to static load while in a particular liquid or gaseous medium. The relationship between applied stress and time to failure graphically plots as a static fatigue curve in which the time to failure increases as the magnitude of the applied load is decreased. Among metals supporting stress, static fatigue behavior is found under three, as yet unrelated, circumstances--in high-strength steel containing 2-10 ppm of hydrogen, in many ferrous and nonferrous metals wetted by specific liquid metals, and in many ferrous and non-ferrous metals immersed in specific aqueous or gaseous media. It is the purpose of this paper to provide argument and evidence that all of these represent instances of the generation of brittle fracture under the action of peculiar environments.

While the delayed failure characteristics of hydrogen-charged steels are well known by virtue of recent work (1), similar behavior brought on by wetting with liquid metals is quite new. Figure 1 illustrates the time-stress dependence of fracture of a hardened 4130 steel wetted by molten lithium at 200°C (2). Similar behavior (2) has been found for high-strength aluminum alloys wetted by mercury amalgams and for 70/30 brass wetted by mercury. The fractures observed are generally intergranular except where the grain structure is elongated by virtue of inhibited grain growth or cold work. It has been shown that this embrittlement initiates at the liquid-solid interface and, although the liquid metal follows the crack, diffusion--either bulk or grain boundary--does not precede the fracture process.

* Metals Research Division, Armour Research Foundation, Chicago, Illinois.

It is apparent that under these conditions of test, where brittle fracture occurs near the yield point, both body-centered and face-centered cubic metals obey the above mentioned Stroh-Petch relationship. Furthermore, from measured values for K , the interfacial energy of solid iron with respect to liquid lithium is about 730 ergs/cm^2 and of solid 70/30 brass with respect to liquid mercury is about 280 ergs/cm^2 . For comparison, the accepted surface energy of 70/30 brass with respect to its own vapor is about 1500 ergs/cm^2 . This provides reasonable grounds for postulating that, in both instances, embrittlement has its fundamental origin in the reduction of surface energy associated with fracture. Moreover, the supply of adsorbing species can come from either the interior atomic interstices of a metal or from an external environment.

Given that hydrogen embrittlement, liquid metal embrittlement, and stress-corrosion cracking have common attributes of delayed failure or static fatigue; given that hydrogen embrittlement and liquid metal embrittlement in continuous loading tensile testing show trends of fracture stress versus a grain size function in accordance with the Stroh-Petch model for the generation of brittle fracture, it is a natural sequence of logic to evaluate whether metals immersed in common stress-corrosion media will obey the same pattern of behavior.

The generation of cracking in a stress-corrosion medium under conditions of continuous loading in tension does not seem to have been studied heretofore. Preliminary experiments in which tensile specimens, while in a stress-corrosion medium, were rapidly loaded to arbitrary stress-levels, unloaded, and examined demonstrated that cracking did occur at critical and reproducible stress levels which were well below those encountered in air. The cracks were many in number but very shallow. One must conclude that the propagation of cracks over large distances involve factors in addition to those responsible for initiation. This will be discussed further. At this point, it must be recognized that the tensile test experiments relate to the conditions for the initiation of brittle fracture in a stress-corrosion medium.

Experimental Procedures

Experiments were conducted on a commercial grade of type 304 austenite stainless steel and on a laboratory-produced, binary alloy of magnesium with aluminum. A chemical analysis of the latter is given in Table I.

By a wide variety of cold working and annealing treatments quantities of stainless steel bar stock were produced with grain sizes varying between 2 and 520 grains/mm². From these, cylindrical tensile specimens were machined having gage sections of dimensions 2 in. long x 0.250 in. diameter. The gage sections were all polished to a high finish. Tensile tests were performed both in air and in an aqueous solution maintained at 150° ± 1°C. The stress-corrosion liquid was held in a glass assembly from which the threaded shoulders of the test specimen protruded at either end. To prevent corrosion at the air-liquid interface, the upper portion of each specimen was coated with an epoxy resin which was unaffected by the MgCl₂ solution. Temperature was established and maintained by a heating element wrapped around the glass assembly. Specimens were immersed in the stress-corrosion liquid for about one hour before testing, this time period being necessary to establish an isothermal condition. Load was applied at a rate of 200 lb per minute.

The Mg-Al alloy was induction-melted and cast into 1 lb ingots. The ingots were homogenized for 30 hours at 410°C and water quenched. Portions of the pre-machined ingots were extruded to 0.4 in. diameter rod at 340°C providing a reduction of about 88%. In this condition, the structure as solution treated was single phase with no evidence of nonequilibrium intermetallic compound. By variation in annealing cycle, quantities of bar stock were obtained with grain sizes ranging from 8 to 1400 grains/mm². All specimens were solution treated and water quenched to retain the single-phase state. Tensile specimens were machined therefrom with gage dimensions: 2 in. long x 0.250 in. diameter. Specimens for test were immersed in an aqueous stress-corrosion solution containing 35 gm NaCl and 20 gm K₂CrO₄ per liter of water. The solution was maintained around the gage section of the tensile specimens by a simple glass tube and rubber stopper assembly. All tests were conducted at room temperature. On the average, the specimens were in contact with the

in the range derived for both hydrogen and liquid metal embrittlement and expected for brittle fracture.

Discussion

The work herein presented reveals that the three circumstances--hydrogen, liquid metal and aqueous solution embrittlement--which produce delayed brittle failure have a common linear dependency of brittle fracture stress on the $d^{-1/2}$ function. Furthermore the slopes of these linear plots of data can be interpreted in terms of reduced surface or interfacial energy as the dominant factor in causing brittle fracture in otherwise ductile metals. The extension of this thesis to embrace the phenomenon of stress-corrosion cracking poses certain questions which at this point can only be discussed in concept.

One must first consider whether this model has effectively eliminated corrosion or electrochemical processes as operative factors. Probably not. It seems reasonable to suggest that electrochemical processes are necessary and responsible for the removal of existing films which prevent adsorption of the critical ion species. This removal need only be localized to serve the purpose. At higher stress levels, electrochemical processes may serve to prevent healing of intervening oxide films ruptured mechanically during loading. The literature on stress corrosion is replete with detailed studies of the relationship between electrode potential measurements preceding and during the fracture process. It has always been assumed that the demonstration of such a relationship proved that the fracture event was electrochemical in origin. In the present hypothesis, electrochemical processes including electrode potential measurements relate the conditioning or removal of the oxide intervening films which prevent adsorption of available ion species.

Electrochemical processes may even be responsible for the generation of the critical ion species and thus also, indirectly, be the controlling factor in the rate of crack propagation. The adsorbing species cannot be identified by present experiments. The Mg^{++} , Cl^- , H^+ , OH^- ions are all suspects, and special ion species may result from breakdown of the oxide film. Work is in progress on various media with the expectation that the operative ion species can be identified by a process of elimination.

It is curious that, while brittle cracks can easily be initiated on continuous loading, they will not propagate very far even at higher stresses. There have been opinions expressed that stress corrosion may be regarded as a two-stage process wherein localized corrosion takes place at susceptible boundaries creating sharp pits which act as stress raisers and the sharpness of the cracks and their depth permit the continuation of cracking without further need for electrochemical processes. Present experience shows that the latter stage is not real. Specimens of stainless steel, which on continuous loading in a stress-corrosion environment produced brittle surface cracks, were subsequently pulled in air to fracture. It was apparent in every case that the initiated cracks did not propagate in a brittle fashion in air. The cracks opened up rather than extended, and failures were clearly ductile. This may be seen in Figure 7. One is forced to the conclusion that the conditions which exist in the process of initiating a brittle crack must persist in its propagation until the localized stress has risen to the ultimate tensile strength. Thereafter, of course, ductile fracture is the faster process.

The limitation of crack depth experienced in continuous loading experiments leads one to the supposition that crack propagation is governed by the rate of supply of the adsorbing ion species to the root of the crack. This is not a problem in hydrogen or liquid metal embrittlement because, in both cases, the adsorbing species have very high mobilities. Depending on the magnitude of the rate of supply, the cracks may progress at a uniform velocity or discontinuously when the rate is very slow and a critical accumulation is needed.

There must be some question about the nature of the obstacle responsible for dislocation pileup and consequent crack nucleation at a liquid-solid interface. A simple series of edge or screw dislocations would be expected to dissipate as shear strain at a free surface. However, the work of Low and Guard (7) on silicon ferrite supplies a suitable mechanism. They have demonstrated that dislocation loops radiating from an internal source can leave at the surface remnants of the loops which translate in the plane of the surface and pile up against grain boundaries at the surface. This essentially reduces the problem to two dimensions. The intersection of these remnants with the surface constitute the points of etch pit formation, and the movement and multiplication of these can and have been studied in terms of the lines of etch pits on

pre-strained large-grained specimens. Micrographs of these are shown by Low and Guard.

A dislocation-surface energy model cannot yet be applied to analysis of delayed failure experiments because the function of time in the dynamics of dislocation assemblies under constant stress has not yet been sufficiently treated. For the present, the further exploitation of this model will have to be confined to continuous loading experiments.

Acknowledgment

This work has been supported by a research contract from the Office of Naval Research. Their encouragement and support is gratefully acknowledged.

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TABLE I
COMPOSITION OF MAGNESIUM-ALUMINUM ALLOY

| Element | Analysis, weight per cent |
|-----------|---------------------------|
| Aluminum | 5.56 |
| Zinc | <0.05 |
| Silicon | 0.08 |
| Magnesium | balance |

TABLE II
THE EFFECT OF STRESS UPON CRACKS
IN A MAGNESIUM-ALUMINUM ALLOY

| Specimen Grain Size | Stress, psi | Number of Cracks* | Depth of Largest cracks, mm |
|---------------------|-------------|-------------------|-----------------------------|
| Small | 19,300 | None | --- |
| | 23,000 | 129 | 0.25 - 0.3 |
| | 23,600 | 276 | 0.5 |
| Medium | 19,200 | 16 | 0.2 |
| | 20,500 | 61 | 0.3 |
| Large | 10,000 | None | --- |
| | 12,500 | 7 | 0.15 |
| | <20,000 | 45 | 0.5 - 0.7 |

* Longitudinal section of 2 in. gage length.

TABLE III
SUMMARIZED DATA ON SURFACE ENERGIES

Type 304 Stainless Steel

| | |
|--|---|
| Shear Modulus | 78.5×10^{10} dynes/cm ² |
| K (in air at 150°C) | 1.45×10^8 dynes/cm ^{3/2} |
| K (in 42w/o MgCl ₂ solution at 150°C) | 5.08×10^7 dynes/cm ^{3/2} |
| γ (in air at 150°C) | 1280 ergs/cm ² |
| γ (in 42w/o MgCl ₂ solution at 150°C) | 157 ergs/cm ² |

Magnesium-Aluminum Alloy

| | |
|--|--|
| Shear Modulus | 16.81×10^{10} dynes/cm ² |
| K* (in air at 25°C) | 9.1×10^7 dynes/cm ^{3/2} |
| K (in NaCl-K ₂ CrO ₄ solution at 25°C) | 2.1×10^7 dynes/cm ^{3/2} |
| γ (in air at 25°C) | 1737 ergs/cm ² |
| γ (in NaCl-K ₂ CrO ₄ solution at 25°C) | 93 ergs/cm ² |

* Determined by least squares solution.

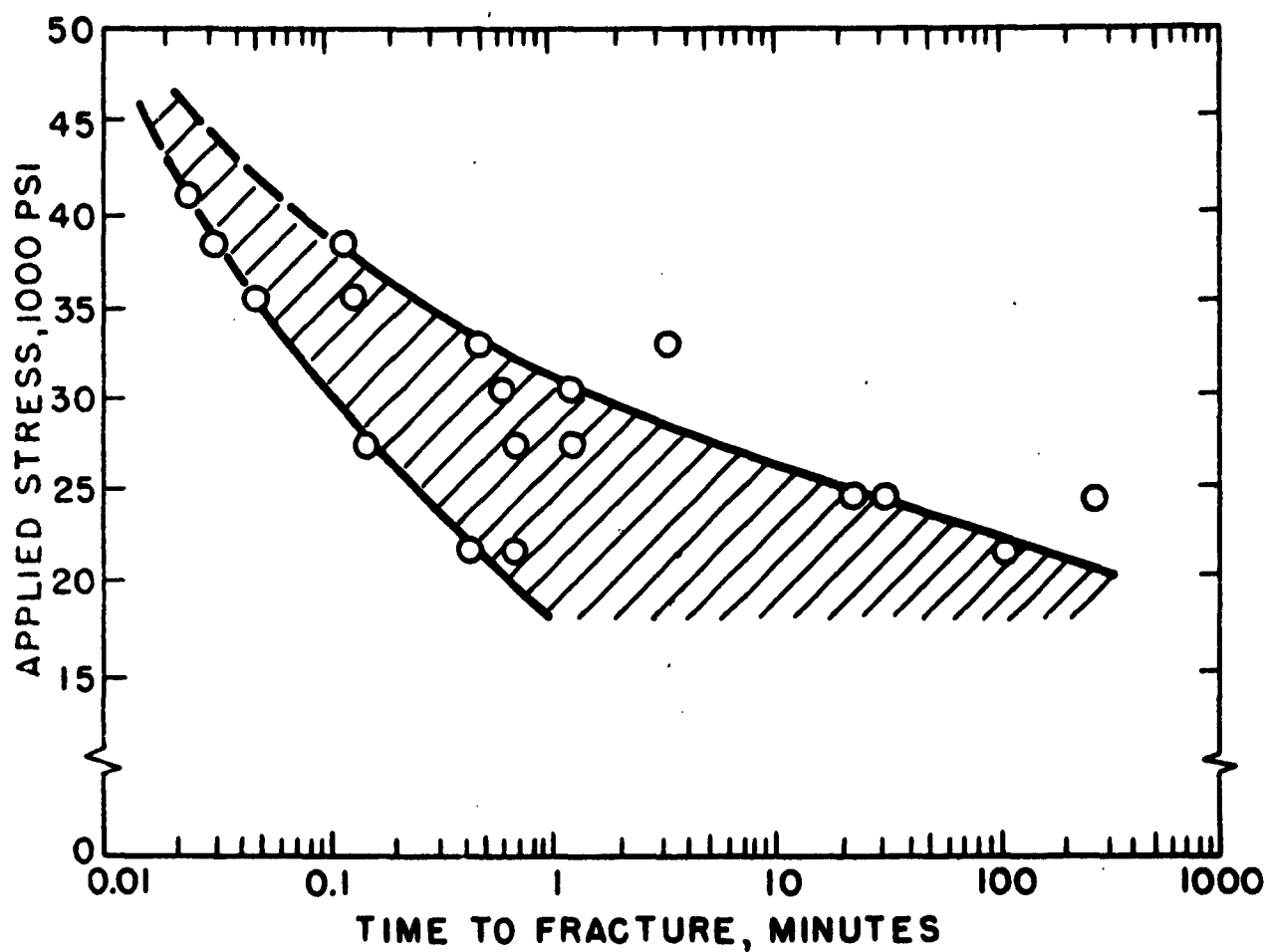


Figure 1 - Delayed failure or static fatigue of SAE 4130 steel at a tempered hardness of Rc44 when wetted with molten lithium at 205°C.

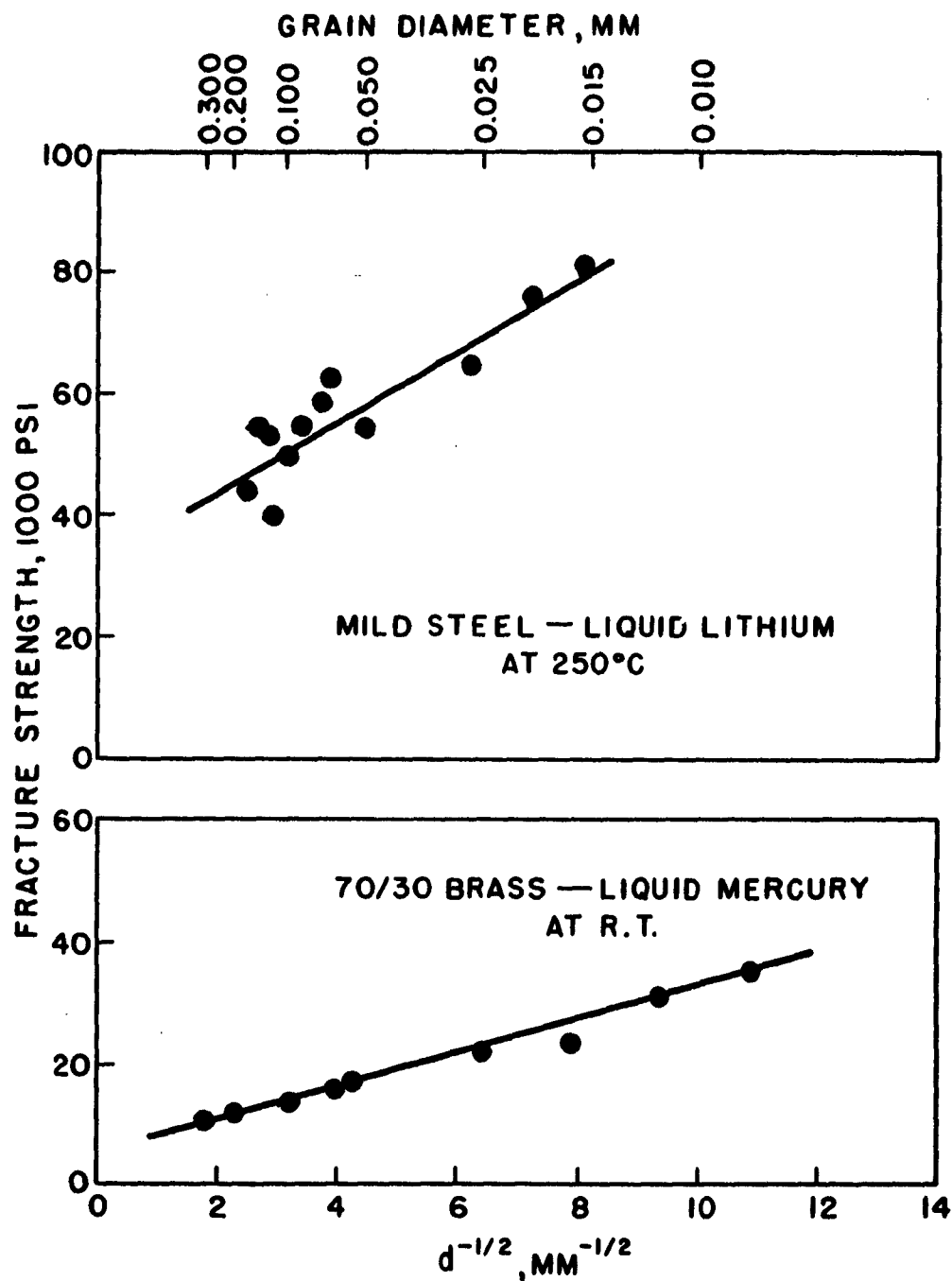
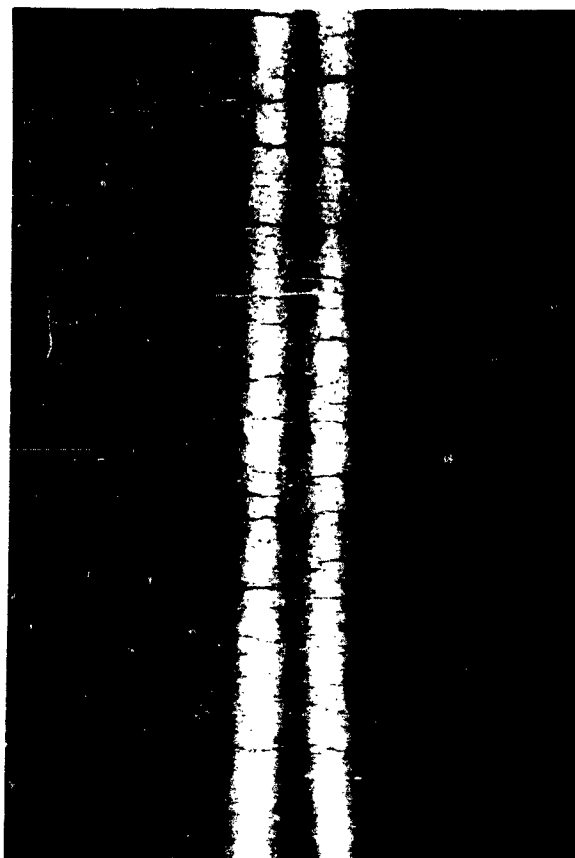


Figure 2 - Dependence of fracture stress on grain size, d , under conditions of wetting by a liquid metal.

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Negative No. 18687

Mag X7

Figure 3 STRESS-CORROSION CRACKS ON STAINLESS STEEL,
CONTINUOUS LOADING IN TENSION IN 42 PER CENT
 MgCl_2 SOLUTION AT 150°C



Negative No. 18688

Mag X10

Figure 4 STRESS-CORROSION CRACKS IN A Mg-6Al SPECIMEN,
CONTINUOUS LOADING IN TENSION IN $\text{NaCl-K}_2\text{CrO}_4$
SOLUTION AT ROOM TEMPERATURE

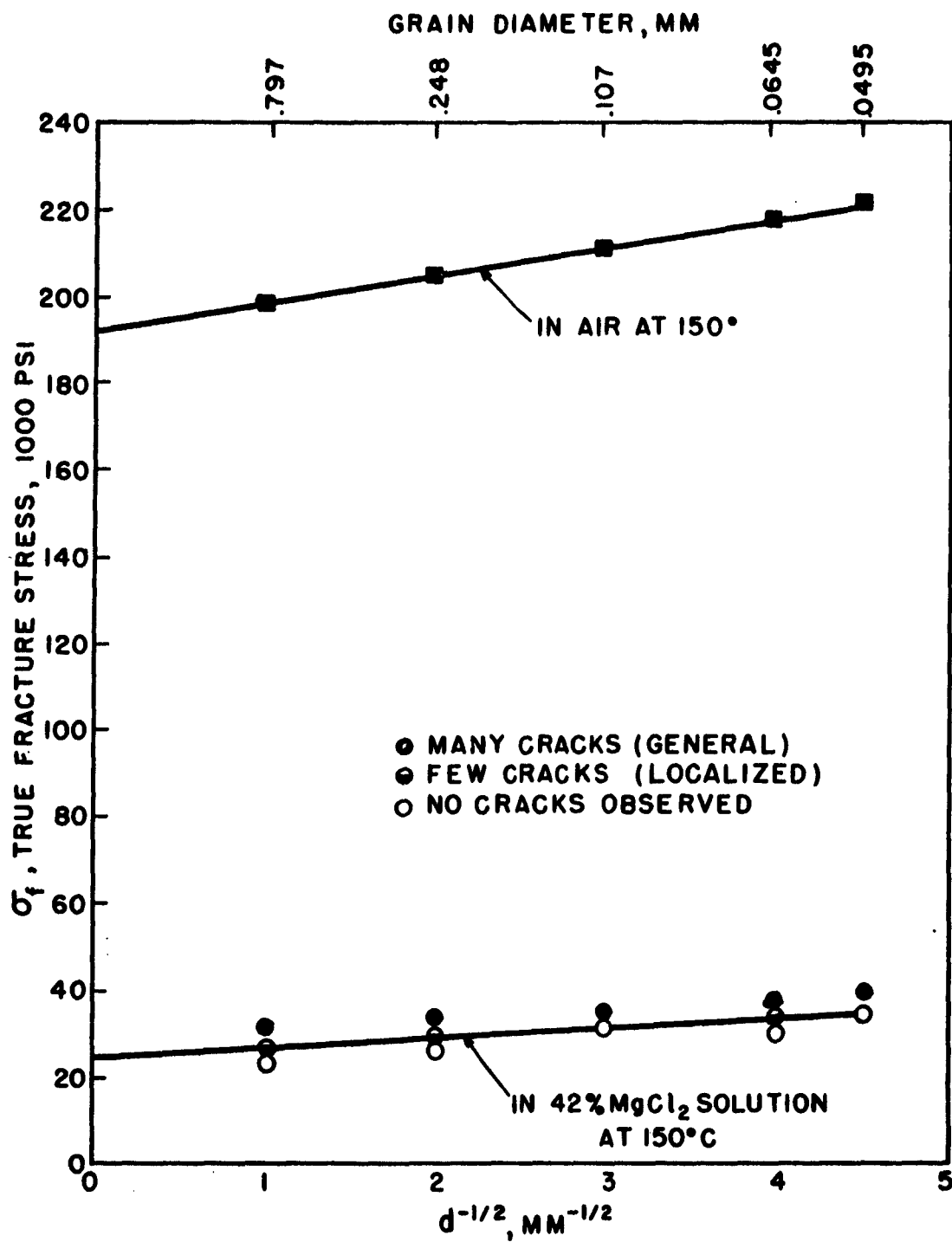


Figure 5 - The fracture stress of stainless steel as a function of grain size.

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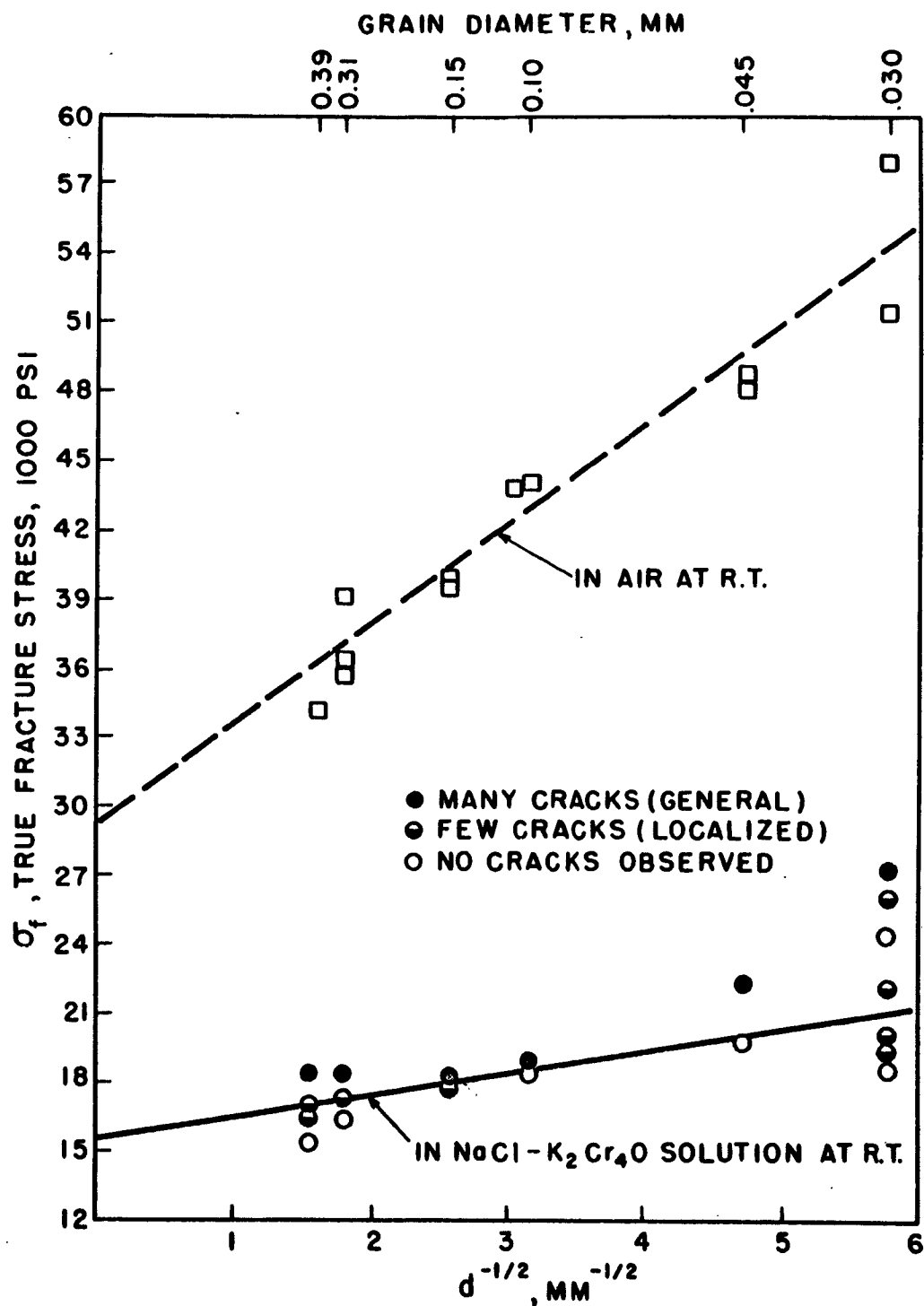


Figure 6 - The fracture stress of a Mg-6Al alloy as a function of grain size.



Negative No. 19488

Mag X250

Figure 7 STRESS-CORROSION CRACKS IN STAINLESS STEEL PRODUCED BY CONTINUOUS LOADING IN TENSION IN 42 PER CENT MgCl_2 SOLUTION AT 150°C ; SPECIMEN REMOVED, AND PULLED TO FRACTURE IN AIR.